Thermodynamical Study on the Heavy-Fermion Superconductor $PrOs_4Sb_{12}$: Evidence for Field-Induced Phase Transition

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We report measurements of low-temperature specific heat on the $4f^2$-based heavy-fermion superconductor $PrOs_4Sb_{12}$. In magnetic fields above 4.5 T in the normal state, distinct anomalies are found which demonstrate the existence of a field-induced ordered phase (FIOP). The Pr nuclear specific heat indicates an enhancement of the $4f$ magnetic moment in the FIOP. Utilizing a Maxwell relation, we conclude that anomalous entropy, which is expected for a single-site quadrupole Kondo model, is not concealed below 0.16 K in zero field. We also discuss two possible interpretations of the Schottky-like anomaly at ~ 3 K, i.e., a crystalline-field excitation or a hybridization gap formation.

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The f-electron-related heavy fermion (HF) systems exhibiting superconductivity had been found only in Ce and U intermetallic compounds. Therefore, the recent observation of the first Pr-based heavy fermion superconductivity (HFSC) in a filled skutterudite $PrOs_4Sb_{12}$ [1] has profound scientific significance.

The $4f^2$ configuration of Pr ions in intermetallic compounds had been considered to be quite stable in view of no observation of strongly correlated electron behaviors until recent studies on $PrInAg_2$ [2] and $PrFe_4P_{12}$ [3–5], in which this picture breaks down. In $PrFe_4P_{12}$, which is also a member of the filled skutterudites, we have shown by specific heat [3], electrical resistivity [4] and de Haas-van Alphen (dHvA) effect measurements [5] that HF behaviors appear in high fields where a nonmagnetic ordered state, probably of quadrupole origin, is suppressed. To our knowledge, $PrFe_4P_{12}$ is the only system in which such definitive evidence for the $4f^2$-based Fermi-liquid HF ground state has been obtained.

Compelling evidence for the HFSC in $PrOs_4Sb_{12}$ was given by a large specific heat jump $\Delta C/T = 0.5$ J/K^2 mol at $T_c = 1.85$ K on a pellet of compressed powdered single crystals [1]. The jump is superimposed on a Schottky-like anomaly appearing at ~ 3 K. Bauer *et al.* attributed this peak to a doublet-triplet ($\Gamma_3 - \Gamma_5$ in O_h-type notation) crystalline-electric-field (CEF) thermal excitation, combining with their magnetic susceptibility $\chi(T)$ and inelastic neutron scattering data. Since the Γ_3 non-Kramers doublet ground state has quadrupole degrees of freedom, they pointed out a possibility that the HF behavior is associated with a quadrupolar Kondo effect [6] on the Pr-ion lattice. In order to confirm this scenario, it is essentially important to clarify how the entropy $R \ln 2$ associated with the Γ_3 ground state is released and whether any residual entropy is hidden far below T_c or not.

In this letter, we report two important findings in $PrOs_4Sb_{12}$ based on specific heat and magnetization measurements on high-quality single crystalline samples: (1) clear evidence for the existence of a field-induced ordered phase (FIOP) and (2) a confirmation of no anomalous entropy concealed below 0.16 K in zero field.

Single crystals of the filled skutterudite $PrOs_4Sb_{12}$ and the reference compound $LaOs_4Sb_{12}$ were grown by Sb-flux method [7]. The raw materials were 4N(99.99% pure)-Pr, 4N-La, 3N-Os and 6N-Sb. No impurity phase was detected in a powder x-ray diffraction pattern. The lattice parameter was determined to be a=9.301 Å for $PrOs_4Sb_{12}$ and a=9.306 Å for $LaOs_4Sb_{12}$. The observation of the dHvA oscillations in both compounds [7] ensures high-quality of the samples. The electrical resistivity $\rho(T)$ for $PrOs_4Sb_{12}$ shows qualitatively the same behavior as reported in ref. [1]. No Kondo-like behavior is visible in $\rho(T)$ although we cannot conclude whether any such behavior exists or not in the small 4f-electron contribution $\rho_{4f}(T)$ estimated by subtracting $\rho(T)$ of $LaOs_4Sb_{12}$. Specific heat $C(H,T)$ for $H \parallel \langle 100 \rangle$ was measured by a quasiadiabatic heat pulse method described in ref. [8] using a dilution refrigerator equipped with an 8-T superconducting magnet. The temperature increment caused by each heat pulse is controlled to be $\sim$2%. The bulk magnetization $M(\mu_0 H \leq 7 \text{ T}, T \geq 1.9$ K) was measured with a Quantum-Design superconducting quantum-interference device (SQUID) magnetometer.

Figure 1 shows the C-vs-T data for $H \parallel \langle 100 \rangle$. In zero field, the data exhibit a Schottky-like anomaly with a maximum of 6.82 J/Kmol at 3.1 K, clearly showing the existence of a low-lying excitation in the f-electron system. In a C/T vs T plot (not shown), the peak appears at 2.1 K with a height of 2.8 J/K^{2}mol, which is 39 % larger than the value reported in ref. [1] for the compressed powdered single crystals, although the overall temperature dependence is similar. In our data, a jump of $\Delta C/T = 0.52$ J/K^2 mol associated with the SC transition is observed at $T_c = 1.81$ K. Details on the SC properties will be reported elsewhere [9].

As Fig. 1 reveals, the anomaly at ~ 3 K is found to be drastically suppressed with increasing magnetic field. This field-sensitive behavior confirms that the low-lying excitation has a magnetic character. In 5 T, a kink appears at $\sim$ 0.7 K and changes the shape into a clear λ-type peak at $T_x = 0.98$ K in 6 T. With further increasing field, the peak in the $C(T)$ curve grows and T_x shifts to higher temperatures. This is the clear thermodynam-

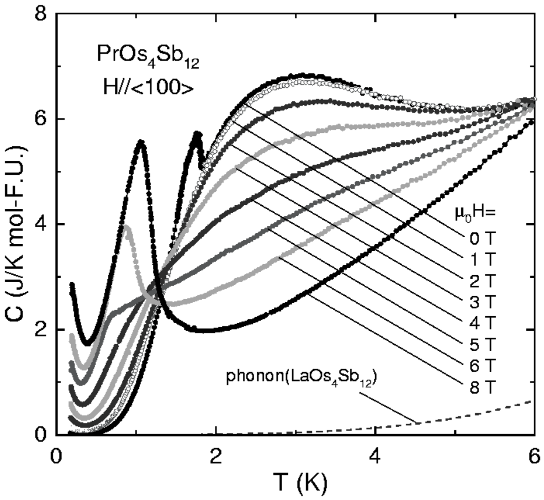

FIG. 1. Specific heat $C(T)$ of $PrOs_4Sb_{12}$ in different magnetic fields. The broken curve represents the phonon part $C_{ph}(T)$ determined from the $C(T)$ data of $LaOs_4Sb_{12}$.

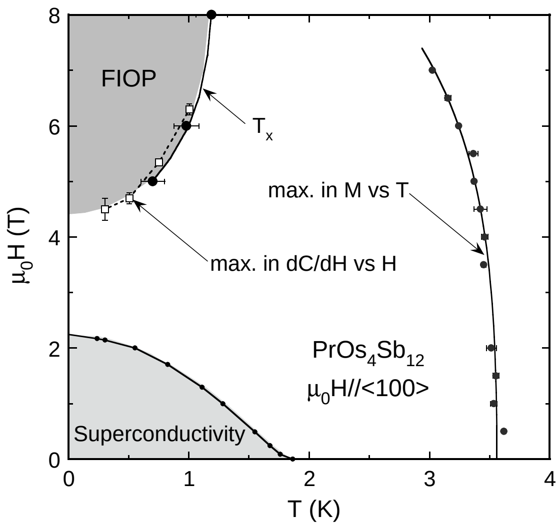

FIG. 2. Magnetic field vs temperature phase diagram. The superconducting boundary is the data from ref. [1]

ical evidence for the existence of a field-induced ordered phase (FIOP) in $T < T_x$. The field variation of T_x is plotted in a H-vs-T phase diagram of Fig. 2.

To estimate the phonon contribution to the specific heat, C_{ph}, we measured $C(T)$ of a single crystal $LaOs_4Sb_{12}$. The obtained $C_{ph}(T)$ is shown in Fig. 1. Negligibly small and smoothly-increasing C_{ph} below 4 K strongly indicates that $4f$ electrons play essential roles in both the Schottky-like anomaly at ~ 3 K and the FIOP below T_x in $PrOs_4Sb_{12}$.

An upturn in $C(T)$ below 0.5 K developing with magnetic field is due to the nuclear Schottky contribution (C_n). The observed C_n is mostly caused by Pr nuclei (nuclear spin $I = 5/2$ for ^{141}Pr with the natural abundance of 100%) because of the strong intrasite hyperfine coupling between the nucleus and $4f$-electrons on the same

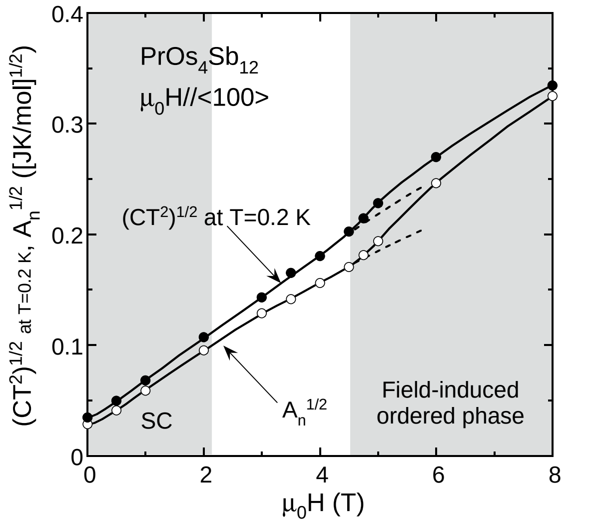

FIG. 3. Magnetic field dependence of estimated $A_n^{1/2}$ in the nuclear specific heat $C_n = A_n/T^2$. $(CT^2)^{1/2}$ at $T = 0.2$ K is also shown to provide an upper bound for $A_n^{1/2}$. The lines are guides to the eye.

Pr ion. This feature allows one to use C_n as an on-site probe for the Pr $4f$ magnetic moment; utilizing this, we have demonstrated that the ordered state in $PrFe_4P_{12}$ appearing below 6.5 K is non-magnetic in origin [3]. We analyze the C_n data to obtain information on the $4f$ magnetic moment of Pr ions in $PrOs_4Sb_{12}$, although the situation is complicated compared to $PrFe_4P_{12}$ because of a non-negligible Sb nuclear contribution. In order to separate C_n from C, we tentatively assume

$$C(T) = A_n/T^2 + \gamma T + \alpha T^n \tag{1}$$

at low temperatures. In eq. (1), the first term represents C_n (the sum of all the nuclear contributions in $PrOs_4Sb_{12}$) and the other two terms represent the low-temperature excitation in $C_e(T)$. The field dependence of $A_n^{1/2}$ obtained by fitting below 0.6 K is shown in Fig. 3. To show an upper bound for $A_n^{1/2}$ based on eq. (1), $(CT^2)^{1/2}$ at $T = 0.2$ K is also plotted. The observed zero-field-value of $A_n^{1/2} = 2.9 \times 10^{-2}$ $[\mathrm{JK/mol}]^{1/2}$ is attributable to the Sb nuclei quadrupole contribution 2.87×10^{-2} $[\mathrm{JK/mol}]^{1/2}$, which is calculated from recent ^{121,123}Sb NQR measurements [10]. With increasing magnetic field, $A_n^{1/2}$ increases gradually and shows a slight upward curvature around the boundary of the FIOP. At the upper critical field $\mu_0 H_{c2} = 2.2$ T, no anomaly can be seen. The field-dependent part in the $A_n^{1/2}$ vs H curve is mostly due to the magnetic Pr nuclear contribution; the magnetic contribution from Os and Sb nuclei gives only ~ 1 % of the observed field dependence. This contribution to A_n can be expressed by

$$A_n^{\mathrm{Pr}} = R(A_{hf} m_{\mathrm{Pr}}/g_J)^2 I(I+1)/3, \tag{2}$$

where R, A_{hf}, m_{Pr} and g_J are the gas constant, the magnetic dipole hyperfine coupling constant, the

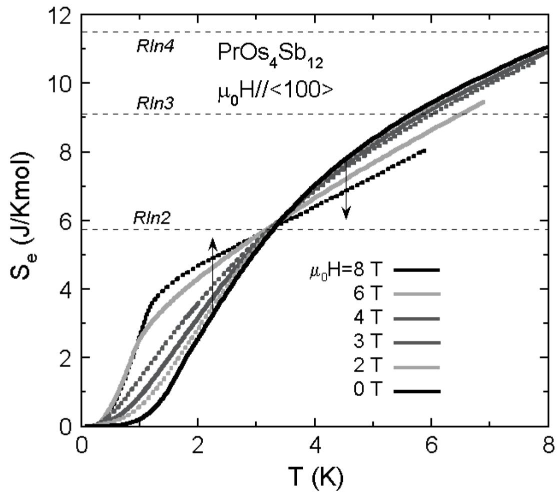

FIG. 4. Electronic part of entropy $S_e(T)$ calculated integrating $C_e(T)/T$ data. Slight adjustment has been made for the data of $H \neq 0$ so that the Maxwell relation $(\partial S/\partial(\mu_0 H))_T = (\partial M/\partial T)_{\mu_0 H}$ is satisfied; see text for the details.

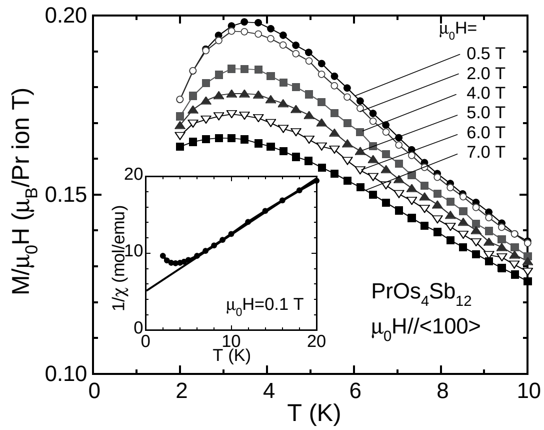

FIG. 5. Magnetization divided by applied magnetic field as a function of temperature. The inset shows the temperature dependence of inverse magnetic susceptibility.

site-averaged magnitude of the Pr magnetic moment $g_J(\overline{|\langle J_z\rangle|^2})^{1/2}$ and the Landé g-factor, respectively. Therefore, the field-dependent part of $A_n^{1/2}$ in Fig. 3 reflects the m_{Pr} vs H curve. Using $A_{hf} = 0.052$ K, which was determined for $\mathrm{PrFe_4P_{12}}$ [3] and is consistent with theoretical calculations [11,12], the experimental value $A_n^{\mathrm{Pr}} = 0.105$ JK/mol for $\mu_0 H = 8$ T leads to an estimation $m_{\mathrm{Pr}} = 1.01\ \mu_B$/Pr in this field. The upturn at ~ 4.5 T in $A_n^{1/2}(H)$ compared to a smooth extrapolation from the lower fields indicates that m_{Pr} (and probably also M) is enhanced in FIOP.

An enhancement of M in the FIOP is expected independently from the Ehrenfest's theorem:

$$\Delta(\partial M/\partial T)_H = -(\Delta C/T_x)(dT_x/d(\mu_0 H)), \qquad (3)$$

which should be satisfied at the second-order phase boundary of the FIOP. Since dT_x/dH is positive in the measured field range as shown in Fig. 2, $\Delta(\partial M/\partial T)_H$ should be negative; this feature was actually observed in a recent low-temperature magnetization study [13]. For $\mu_0 H = 6$ T, $\Delta(\partial M/\partial T)_H \simeq -0.04\ \mu_B$/Pr K is calculated.

We obtained the temperature dependence of the electronic part of entropy $S_e(T)$ by numerically integrating the data of $C_e/T \equiv (C - C_n - C_{ph})/T$ vs T. Since our measurements are made above 0.16 K, only $\Delta S_e(T) \equiv S_e(T) - S_e(0.16\ \mathrm{K})$ can be obtained from the present study. Therefore, we tentatively plot $S_e(T)$ in Fig. 4 putting $S_e(0.16\ \mathrm{K}) = 0$ for each magnetic field; if $C_e/T \sim 0.047$ J/K^{2}mol at 0.16 K in zero field continues down to $T = 0$, an error caused by this assumption would be $S_e(0.16\ \mathrm{K}) - S_e(T=0) = 7 \times 10^{-3}$ J/K mol, which is negligibly small. As a next step, the $S_e(T)$ curves for $\mu_0 H \neq 0$ T are vertically shifted so that the Maxwell relation:

$$(\partial S_e/\partial(\mu_0 H))_T = (\partial M/\partial T)_{\mu_0 H} \qquad (4)$$

is consistently satisfied at 5 K by both the S_e and M data shown in Fig. 5. The maximum shift of S_e required for the adjustment is 0.02 J/K mol, which is invisible in Fig. 4. Two $S_e(T)$ curves for adjacent magnetic fields in Fig. 4 cross at a temperature ($3 \sim 3.5$ K), which coincides with the maximum temperature of the corresponding M/H vs T curve shown in Fig. 5, demonstrating the consistency of the present data with eq. (4). We also confirmed that results of magnetocaloric effect measurements are consistent with the S_e data shown in Fig. 4.

There are two possible interpretations for the Schottky-like anomaly appearing at $\sim$ 3 K: (1) a CEF excitation superimposed on a moderately mass-enhanced quasiparticle excitation, or (2) a strongly energy-dependent quasiparticle excitation itself. In the case (1), γ is of the order of 10^{-1} J/K^{2}mol and $\Delta C/\gamma T_c$ is not far from the BCS value, while in the case (2), $\gamma(T)$ has a strong temperature dependence and $\Delta C/\gamma(T_c)T_c \simeq 0.1$ is quite smaller than the BCS value.

In the case (1), the maxima at $3 \sim 3.5$ K in the M/H-vs-T curves as well as the field-sensitive behavior of the Schottky peak indicate that the CEF first excited state lying at $E_1/k_B \sim 8$ K is magnetic. In the CEF model proposed by Bauer *et al.* [1], where the $\Gamma_3 - \Gamma_5$ excitation leads to the Schottky peak in $C(T)$ at 3 K, an entropy of $R\ln 2$ associated with the Γ_3 ground state should be hidden below 0.16 K in zero field, if it is assumed that $4f$ electrons are well localized. Since applying magnetic field should cause a small but detectable splitting of the Γ_3 doublet (e.g. an energy splitting $\Delta E = 1.5$ K in 4 T is calculated using the CEF parameters of $x = -0.72$ and $W = -5.44$ K from ref. [1]), a new low-T peak would appear in $C(T)$ and thereby the hidden entropy would be released, i.e., $S_e(0\ \mathrm{T}) - S_e(4\ \mathrm{T}) \simeq R\ln 2$ at 0.16 K. Our

S_e data shown in Fig. 4 are clearly against this scenario, and we conclude that no anomalous entropy is concealed below 0.16 K in zero field. [14]

If a Γ_1 singlet is the CEF ground state, the first excited state should be a magnetic triplet Γ_5 (Γ_4 in T_h notation [15]). Observed anisotropy in M, i.e., $M(H//\langle 110\rangle) \simeq M(H//\langle 111\rangle) = 1.110\ \mu_B/\mathrm{Pr} > M(H//\langle 100\rangle) = 1.095\ \mu_B/\mathrm{Pr}$ at 1.9 K in 7 T, asserts the $\Gamma_1 - \Gamma_5$ level scheme (see Fig. 7 of ref. [3] for a calculation of M for a single-site Pr ion), although the absence of clear downward curvature in $M(H)$ curves for all the three field directions (see Fig. 5 for $H//\langle 100\rangle$) is not in agreement with the simple CEF predictions not only for the $\Gamma_1 - \Gamma_5$ but also for the $\Gamma_3 - \Gamma_5$ level schemes. The $\Gamma_1 - \Gamma_5$ level scheme is consistent with the fact that S_e is lower than $R\ln 4$ at 8 K and increasing gradually. The maximum value of C at ~ 3 K is smaller than 8.51 J/K mol expected for the singlet-triplet Schottky peak, [16] indicating that the triplet excited state has a energy dispersion due to Pr-Pr magnetic interactions.

The FIOP appears in the field region where one level out of the Γ_5 triplet goes down due to the Zeeman effect and effectively degenerates with the ground state. Actually, S_e shown in Fig. 4 increases with increasing field below ~ 3 K and seems to show a tendency of saturation (plateau) at $R\ln 2$ when the FIOP is fully developed in fields above 8 T. Therefore the formation of the FIOP probably needs the degree of freedom possessed by the quasi-degenerate doublet formed in the high fields. We speculate that the order parameter is of an antiferroquadrupole accompanied by a field-induced antiferromagnetism (AFM), as observed in CeB_6 [17,18] and TmTe [19,20]. In these compounds, the quadrupole ordering temperature shifts to higher temperatures with increasing field. In $PrOs_4Sb_{12}$, the negative Curie-Weiss temperature $\Theta_{\mathrm{CW}} = -6.6$ K determined below 20 K as shown in the inset of Fig. 5 indicates the existence of AFM correlations. Therefore, by field-induced AFM components, the FIOP could be energetically stabilized leading to $dT_x/dH > 0$. Note that preliminary data of $d\rho/dT$ indicate that dT_x/dH changes to negative above 10 T [7], as similarly observed in both CeB_6 and TmTe.

In the case (2), the Schottky-like peak in $C_e(T)$, similar to the one observed at ~ 7 K in CeNiSn [21], implies the existence of a hybridization gap in the energy spectrum of the renormalized quasiparticle excitations in $PrOs_4Sb_{12}$ [22]. From the $C_e(T)$ data, the size of the gap is roughly estimated to be $\Delta_K/k_B \sim 8$ K, which is four times larger than T_c. This fact suggests that the superconductivity appears in the temperature region where the gap structure is well developed. Figure 1 clearly shows that the gap structure is sensitive to magnetic field and is destroyed above ~ 5 T. In these fields, the quasiparticle density of states at the Fermi energy increases and consequently developed RKKY-type AFM interactions would help to form the FIOP.

For a clear distinction between the cases (1) and (2), no decisive experimental facts are available at this stage. However, this point should be clarified to understand the first $4f^2$-based HFSC in $PrOs_4Sb_{12}$.

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Note added.- The effect of the deviation from the T^{-2}-dependence of the Pr nuclear contribution becomes non-negligible in high fields (*e.g.*, see Fig. 1 in Ref. 23). If one follow the analysis described in Ref. 3, $m_{\mathrm{Pr}} = 1.15\mu_{\mathrm{B}}/\mathrm{Pr}$ is obtained in 8 T. Note that the long heat pulse (~ 1 min), the longtime T-response measurement (> 10 min) and our data fitting procedure fully dealing with the tau-2 effect caused by long nuclear-spin-lattice-relaxation times allow us the precise measurements of the nuclear contribution. After completion of this paper, we became aware of the result of Maple *et al.* who observed anomaly in ρ corresponding to the FIOP. [24]

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close to 6.33 J/K mol expected for a singlet-doublet Schottky peak, such a level scheme formed by a splitting of a Γ_5 triplet ground state seems to be possible. However, this level scheme requires a site-symmetry-lowering of the Pr^{3+} ions from the cubic symmetry and this possibility disagrees with a neutron diffraction study at room temperature [K. Oikawa *et al.*: private communication] and the absence of any splittings of the ^{121,123}Sb NQR signals at low temperatures [10].

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